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CONTENTS

Kōhei HOSINO: Studies on Synthetic Polyamide (V). Precipitability and Melt Viscosity 171

Nobuyuki TANAKA: Studies on Nickel and Cobalt in Mineral Springs. III. Nickel Content of Some Mineral Springs and Their Deposits 177

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(JES B. No. 5)

Studies on Synthetic Polyamide (V).[1] Precipitability and Melt Viscosity.[2]

By Kōhei HOSINO.

(Received September 5, 1944.)

Introduction. The present investigation attempts to find the relation between precipitability and solution viscosity, and the relation between melt viscosity and solution viscosity for the polyamide derived from ε-aminocaproic acid.

Methods.

Materials. Pure ε-caprolactam was prepared, isolated and purified by vacuum distillation as described in my second paper.[3] One mole of ε-caprolactam which had dissolved various quantity of pure butyric acid (Takeda Chemicals Co., b.p. 160–162°) was placed in an autoclave and heated at 250–270° under the pressure 15 kg./cm.²of hydrogen for 23 hours. Uniformity of temperature all around the autoclave was established by heating in salt bath of a mixture of potassium nitrate and sodium nitrate in mole ratio. Thus the materials No. 1–17 polymer in Table 1 were prepared, and No. 18, without butyric acid, was prepared by evacuating during the last period of the polymerization.

Solution Viscosity. The solution viscosity was determined on the solutions of the polymer in freshly redistilled *m*-cresol (b.p. 201–202°). The Ostwald viscosimeter was thermostated in a water bath at 30±0.02°. Kinetic energy corrections were never important as the efflux time for about 10 c.c. of the solvent was longer than 120 seconds. The viscosities were all measured at concentration of c=0.4000±0.0020 g. per 100 c.c. of solution. The viscosity of the pure solvent η_0 and that of the solution η_1 are related to intrinsic viscosity $[\eta]$ by

$$[\eta] = \frac{ln\frac{\eta_1}{\eta_0}}{c}.$$

Precipitability. Solutions of 1.0000(±0.0008) g. of the polyester in 25 c.c. of *m*-cresol were maintained at 20.0° in a thermostat and were slowly titrated, under isothermal conditions, with heptane (Takeda Chemicals Co., b.p. 81–91°) from a calibrated microburette. The nonsolvent, heptane, was added with constant and vigorous agitating during the addition. A translucent turbidity indicated the end-point. The end-points were

(1) (IV), this Bulletin, **19**(1933), 153; 158.
(2) *J. Chem. Soc. Japan*, **65**(1944), 419.
(3) This Bulletin, **18**(1943), 105.

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sharp and could be reproduced within 1%, but the constancy of temperature during the titration was essential, and for instance the titre varied as follows as the temperature varied.

Temperature, °C.	5	10	15	20	25	30
Heptane, c.c.	26.20	28.90	29.60	31.10	32.30	33.70

The precipitability γ is the fraction of the total volume of non-solvent at end-point for a given constant initial weight concentration of polymer.

Melt Viscosity. Small steel spheres carefully selected for uniformity which had been previously heated at desired temperature were dropped into 27 mm.×300 mm. glass tube containing the melt of the polyamide. The tube was placed in a salt bath which was completely within an electric furnace. Observing the ball with strong illumination, its time of fall through 50 mm. distance was measured by means of a stop watch. The temperature was controlled, a sealed mercury regulator and a thermometer and transformers being used. The temperatures of the measurement were (220±0.5°), 240±0.5°, 260±0.5°, and 280±0.5°. The test showed that the polyamide did not decompose nor change during three hours at these temperatures in the atmosphere of carbon dioxide; they were entirely stable over the measuring period. Melts were freed from gas bubbles by standing. Melt viscosities μ were calculated by Dorr and Roberts' equation,[4]

$$\mu = \frac{g}{18} \frac{d^2(\rho' - \rho)}{\left(1+2.1\frac{d}{D}\right)\left(1+\frac{R}{12}-\frac{R^2}{960}\right)},$$

where g is the gravity constant, d is the diameter of steel balls, ϱ' is the density of steel balls, ϱ is the density of the melted polymer, D is the diameter of the glass tube, v is the velocity of ball fall, and $R(=dv\varrho/\mu)$ is Reynold's number. To the data of d and ϱ' at room temperature, corrections were applied by using the thermal expansion constant. From the volume occupied by melted polymer of known weight, ϱ was determined.

$$\rho = 1.083(240°),\ 1.076\ (260°) \text{ and } 1.070\ (280°)$$

Results and Discussions.

The results of titration and viscosity determination are included in Table 1.

(1) $[\eta]-\gamma$ *Relationship.* The sharp dependence of solubility on solution viscosity or molecular weight are seen in Fig. 1. Higher molecular polycapramide has little solubility, and γ and reciprocal of $[\eta]$ are in linearity in the range of $[\eta]<0.8$,

$$\gamma = 0.521+0.0285/[\eta]. \qquad (1)$$

(4) Dorr and Roberts, *Trans. Am. Inst. Chem. Engrs.* **33**(1937), 106.

In the ragne of $[\eta]>0.8$, this equation is not applicable. It is conceived that $[\eta]$ is proportional to the weight-average degree of polymerization P_w and that P_w is approximately twice the number-average degree of polymerization P_n on highly condensated linear polymers. Therefore equation (1) can be transformed into

$$\gamma = \alpha + \beta/P_n , \qquad (2)$$

where α and β are constants for the given series. This relation has been applied to polystyrene by Schulz,[5] to polyundecanate by Baker,[6] and to polyoxyethylene glycol by Hibbett.[7] Thus it is proved that equation (2) may be applicable to the low molecular weight polycapramide in *m*-cresol when titrated with heptane.

Table 1.

No.	Mole of butyric acid	$[\eta]$	Heptane c.c.	γ	μ poise 280°	260°	240°
1	0	0.7058	31.10	0.554	181.0	266.2	550.8
2	1/800	0.6660	32.30	0.564	115 3	163.1	320.4
3	1/400	0.6358	32.60	0.566	63.8	115.1	179.9
4	1/200	0.5876	34.80	0.582	—	—	—
5	1/100	0 4152	36.20	0.590	19.0	29.2	52.2
6	1/50	0.3715	27.70	0.601	8.1	11.2	15.4
7	1/25	0.2936	44.10	0.622	1.4	2.3	2.8
8	1/10	0.1798	53.10	0.680	0.6	0.7	0.9
9	0	0.6808	32.50	0.565	160.5	233.4	323.0
10	1/800	0.6693	32.80	0.567	83.2	162.6	250.3
11	1/400	0.6032	33.30	0.571	61.1	116.4	192.6
12	1/200	0.5891	35.00	0.583	42.2	96.8	124.5
13	1/100	0.3700	35.30	0.585	13.2	18.3	25.6
14	1/50	0.3185	37.70	0.600	4.5	7.2	19.3
15	1/25	0.2465	42.60	0.630	1.6	2.3	2.8
16	1/10	0.1912	52.20	0.676	—	—	—
17	0	0.8865	28.70	0.534	692 3	1017	1363
18	0	1.0665	27.00	0.521	820.4	1218	1576

(2) $[\eta]$-μ *Relationship.* Log μ and $[\eta]^{\frac{1}{2}}$ are in linear relationship as are shown in Fig. 2, and these straight lines are expressed by the following equations:

$$\left.\begin{aligned} &\text{at } 240^\circ,\ \log \mu = -2.5+6.2\,[\eta]^{\frac{1}{2}} \\ &\text{at } 260^\circ,\ \log \mu = -2.7+6.2\,[\eta]^{\frac{1}{2}} \\ &\text{at } 280^\circ,\ \log \mu = -3.0+6.2\,[\eta]^{\frac{1}{2}} \end{aligned}\right\} \qquad (3)$$

(5) Schulz, *Z. physik. Chem.*, **A179** (1937), 321.
(6) Baker, Fuller and Heiss, *J. Am. Chem. Soc.*, **63** (1941), 2142.
(7) Lowell and Hibbert, *J. Am. Chem. Soc.*, **61** (1939), 1916.

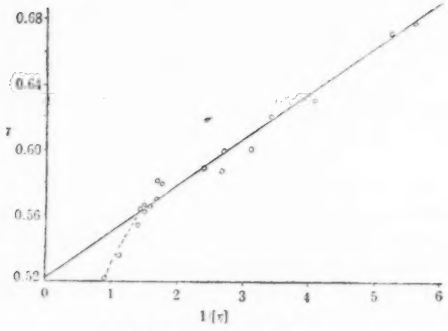

Fig. 1. $[\eta]$-γ curve.

Flory[8] has reported a linear relationship between $\ln\mu$ and $Zw^{\frac{1}{2}}$ on polyester, when Zw is the number of chain atoms in the molecules of weight-average molecular weight, and has applied to molecular weight determination,

$$\mu = A' \, e^{C'Zw^{1/2}} \qquad (4)$$

where A' and C' are constants.

As it has been proved that Zw approximately proportional to $[\eta]$, the equation (3) may be transformed into (4) and (5),

$$\log \mu = A'' + C[\eta]^{\frac{1}{2}}, \qquad (5)$$

where A'' is a constant dependent of temperature, and $C=6.2$.

(3) *The relation between μ and the absolute temperature T.* Typical data are given in Tables 1 and 2, and the results are included in Figs. 3 and 4, where $\log \mu$ is plotted against the reciprocal of absolute temperature T. According to the well-known equation,

$$\log \mu = A''' + B/T, \qquad (6)$$

the observed points in Figs. 3 and 4 must lie on straight lines. The slope of these lines ranges from 2100 to 2500, independent of molecular weight.

(4) *μ-T-$[\eta]$ relationship.* From the equations (5) and (6), we obtain

$$\log \mu = A + B/T + C[\eta]^{\frac{1}{2}}, \qquad (7)$$

where A, B and C are constants. According to the theory of Eyring and Kauzmann[9] on viscosity of large molecules,

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(8) Flory, *J. Am. Chem. Soc.*, **62**(1940), 1057.

(9) Eyring and Kawzmann, *J. Am. Chem. Soc.*, **62**(1940), 3113.

$$\log \mu = ln\frac{Nh}{V} - \frac{\Delta S^+}{R} + \frac{\Delta H^+}{RT}, \qquad (8)$$

where N is Avogadro's number, h is Planck's constant, V is the volume of unit flow of molecule, R is gas constant, ΔS^+ is entropy of activation

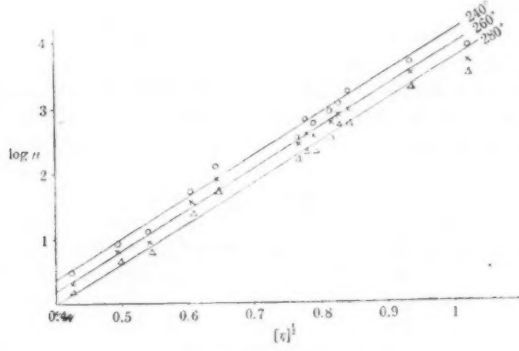

Fig. 2. μ–$[\eta]$ curves.

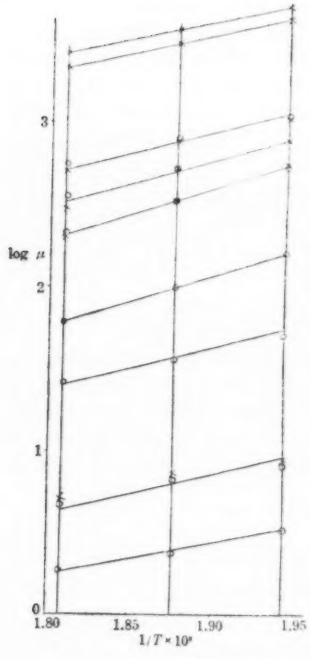

Fig. 3. μ–1/T curves.

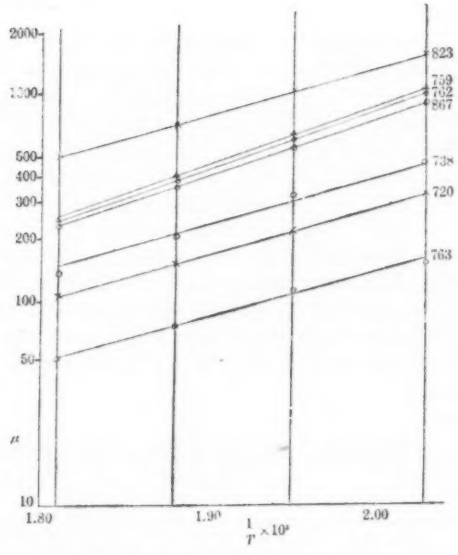

Fig. 4. μ–1/T curves.

for viscous flow, and ΔH^{+} is its energy of activation. Comparing the equations (7) and (8)

$$\Delta H^{+} = 2.3\,RB, \tag{9}$$

and it may be said that $\Delta H^{+}=9.7-11.5$ kcal for polycapramide independent of molecular weight. Flory's data on polyester, $B=1800$ and $\Delta H = 8.0-8.5$ kcal[8]. For polycapramide,

$$\log \mu = -7.0+2300/T+6.2[\eta]^{\frac{1}{2}} \tag{10}$$

This equation is applicable to the polymer of $[\eta]<1$, and is not applicable to that of $[\eta]>1$ nor to that containing three dimensional links, nor to partially oxidized polymer.

Table 2.

Melt viscosity μ of polycapramide in poise.

No.	220°	240°	260°	280°
738	485	347	209	139
720	320	231	150	108
759	1197	645	403	257
762	1125	642	390	255
763	155	111	783	542
823	1680	1160	760	540
867	928	588	349	246

Summary.

A study of polyamide has been attempted on a series of strictly isochemical linear synthetic polyamide derived from ε-aminocaproic acid.

(1) The polymer molecules have been investigated by "equilibrium" interaction with a non-solvent in solution (precipitability γ), kinetic interaction in a dilute solution (solution viscosity $[\eta]$), and kinetic interaction in a condensed polymer phase (melt viscosity μ).

(2) $[\eta]$–γ relationship is established experimentally.

(3) μ–T–$[\eta]$ relationships are established experimentally.

In conclusion, the author wishes to express his sincere gratitude to Mr. A. Karashima and Mr. S. Tashiro for the permission for the publication and for the encouragement, and to Dr. K. Tanemura for his kind guidance throughout this work, and the author desires to thank Messrs. S. Huzii and N. Hisaki for their valuable assistance in the experimental work.

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Studies on Nickel and Cobalt in Mineral Springs. III. Nickel Content of Some Mineral Springs and Their Deposits.

By Nobuyuki TANAKA.

(Received September 8, 1944.)

The author's previous studies[1][2] on the nickel content of mineral springs were confined to that of acid vitriol springs rich in iron. Those poor in iron and high in pH value, for example, the carbonate spring and the common salt spring, are considered to contain smaller quantities of nickel. Their atomic ratio of nickel to iron is also not yet known to us.

After the publication of the last of this series, the author has planned the determination of nickel in mineral waters of all kinds. The study, which had to be given up half-way because of the investigation along the other line, has been published in this report.

Experimental.

Mineral Waters.

Methods for nickel determination. Nickel was determined colorimetrically by measuring the colour of nickelic dimethylglyoxime compound, which develops by the addition of the dimethylglyoxime reagent to nickel compound in the nickelic state. The details of the method were described in the previous paper[1], the outline of which is as follows. Nickel in mineral waters was converted into nickel dimethylglyoxime by the addition of the dimethylglyoxime reagent in the presence of tartaric or citric acid. Nickel dimethylglyoxime was extracted with chloroform, and, in the chloroform layer, was decomposed with dilute hydrochloric acid. After the acid layer was treated with bromine, the dimethylglyoxime reagent was added again, then the colour of nickelic dimethylglyoxime thus developed was measured by the Pulfrich photometer using the filter S45 (450 mμ).

Acid Hydrogen Sulphide Springs.

In the prveious papers the nickel content of acid vitriol springs was represented. The acid hydrogen sulphide springs, however, are considered to belong to another group. The examples taken up here are:

(1) Sirahata no yu, Kusatu.
(2) Netu no yu, Kusatu.
(3) Yubata no yu, Kusatu.

Nickel and iron contents, determined by the colorimetric and the volumetric methods respectively, are:

---

(1) N. Tanaka, this Bulletin, **18**(1943), 201.
(2) N. Tanaka, this Bulletin, **18**(1943), 365.

	Nickel content (γ/l.)	Iron content (g./l.)
(1) Sirahata no yu	less than 2	0.0376
(2) Netu no yu	less than 2	0.0144
(3) Yubata no yu	less than 2	0.0603

Therefore, the atomic ratio of nickel to iron is calculated as follows.

(1) Sirahata no yu	less than 0.51×10^{-4}
(2) Netu no yu	less than $1.3_2\times10^{-4}$
(3) Yubata no yu	less than 0.32×10^{-4}

Carbonate Springs.

The samples taken up here are:

(4) Nanasigure, Iwate Prefecture.
(5) Zyōhōji, Iwate Prefecture.

Both are noted for containing the large quantity of boric acid. They were determined by Dr. K. Kuroda and his co-worker[3] in August, 1941 and reported as follows.

	Temp. (°C)	pH	Content of boric acid (g. B_2O_3/l.)
(4) Nanasigure	16.0	6.4	2.594
(5) Zyōhōji	12	6.5	2.5788

Taking a large amount of the sample waters, the determination of nickel was made. The results obtained:

	Sample taken (l.)	Nickel content (γ)	Nickel content (γ/l.)	Total residue (g./l.)
(4) Nanasigure	11.00	8.55	0.78	11.691
(5) Zyōhōji	9.50	16.9	1.78	18.792

The iron content of Nanasigure, determined colorimetrically, is 131.2 γ/l. The nickel percentage in total residue and the atomic ratio of nickel to iron obtained are as shown in the following.

	Nickel in total residue (%)	Ni/Fe -atomic ratio
(4) Nanasigure	0.67×10^{-5}	0.57×10^{-2}
(5) Zyōhōji	0.95×10^{-5}	——

Simple Cold Springs.

Mamegara-hudō-yu, which is located near Sirakawa, Hukusima Prefecture, was taken up as an example. In this spring the occurrence of nickel had been found with spectrograph.[4] The spring belongs to the simple cold spring, with 12.5°C in temperature and 6.7 in pH value (determined on the 1st of June, 1941). The nickel content, the total and the ignition residues are:

(3) K. Kuroda and T. Tagaya, *Bull. Inst. Phys. Chem. Research* (Tokyo), **21** (1942), 181.
(4) By Prof. Kenjiro Kimura.

Nickel content	6.7_5 γ/l.
Total residue	0.0803 g./l.
Ignition residue	0.0633 g./l.

Therefore, 0.0084% was obtained as the nickel percentage in total residue.

Determined by the colorimetric method, on the other hand, the iron content of this spring was 246 γ/l. and, therefore, the atomic ratio of nickel to iron is 2.6×10^{-2}.

Ikaho, Gunma Prefecture.

At Ikaho, there are many mineral springs of several types. All of these are drawn into a pipe, from which the sample water was taken. Nickel and iron in both of "the filtrate" and "the precipitate" were determined separately, because some precipitates had appeared in the sample waters from being kept on standing for a long time. One litre of the filtrate contains 1.9 γ of nickel and 53 γ of iron, while the precipitate derived from one litre of the water contains 1.8 γ of nickel and 4.44 mg. of iron. From the results, it was known that one litre of the original water contains 3.7γ of nickel and 4.49 mg. of iron. The atomic ratio of nickel to iron, therefore, was calculated as follows.

Ni/Fe-atomic ratio	7.8×10^{-4}

The atomic ratio of nickel to iron in the filtrate is so much larger than that in the precipitate that it is concluded that the nickel remains mostly in the filtrate even after almost all of iron has precipitated from the solution.

Service Water of Tokyo.

The nickel content of the service water of Tokyo was determined for the purpose of estimating the nickel content of river waters. The sample was taken every day from November 14, 1942 to December 2. The nickel, iron and total residue contents shown in the following, therefore, mean the averages of those for some twenty days.

Nickel	1.18 γ/l.
Iron	82.5 γ/l.
Total residue	0.04430 g./l.

From the result, the nickel percentage in total residue and the atomic ratio of nickel to iron are calculated at 0.0026_6% and 1.36×10^{-2} respectively.

Deposits.

The deposits taken for the present investigation are of three types, which are formed from the mineral spring Ikaho. The first (Sample No. 1) is the so-called "ocherous deposit", the second (Sample No. 2) calcareous deposit, and the third (Sample No. 3) also calcareous but with somewhat different appearance.

No. 1 mainly consists of ferric oxide, and is apparently non-crystalline. No. 2 and No. 3 consist mainly of calcium carbonate with a little of ferric

compound, the former of which shows crystalline appearance, while the latter is non-crystalline. X-ray powder photograph of No. 2 agrees with that of calcite type, while that of No. 3, that of aragonite type. It, therefore, becomes clear that the difference of the appearance between No. 2 and No. 3 is due to the difference of their crystalline state, and is attributed to the difference of the condition of formation. The determination of nickel was made in the same way as in the case of the mineral waters, using the filtrates obtained by decomposing the samples with hydrochloric acid. The nickel content of these deposits is shown in Table 1, together with the contents of iron and of insoluble residue (mainly SiO_2).

Table 1.

	No. 1	No. 2	No. 3
Nickel (%)	0.79×10^{-4}	$<2.0\times10^{-4}$	$<2.0\times10^{-4}$
Iron (%)	38.0	2.2	3.2
Insoluble residue (%)	22.08	1.29	0.90
Ni/Fe-atomic ratio	2.0×10^{-6}	$<8.7\times10^{-5}$	$<6.0\times10^{-5}$

The analyses of No. 2 and No. 3 were carried out to find out the difference between the nickel content of No. 2 (calcite type) and that of No. 3 (aragonite type). However, the purpose was not attained owing to the lack of the samples.

Atomic Ratio of Nickel to Iron.

The determination of nickel in mineral waters of several types has been carried out polarographically by K. Heller, G. Kuhla and F. Machek[5]. The nickel content of the common salt spring ("Marienbader Quelle"), according to their report, falls between 8.3 γ/l. and 0.28 γ/l., that of the bitter spring ("Karlsbader Quelle"), less than 0.43 γ/l. and that of the radioactive spring ("Curiequelle"), less than 0.14 γ/l. In the present study, the maximum content of nickel is 6.7_5 γ/l. of the simple cold spring, Mamegara-hudō-yu, while the minimum is 0.78 γ/l. of the carbonate spring, Nanasigure, with the exception of the hydrogen sulphide springs, Kusatu giving less than 2 γ/l. As shown in Table 2 the nickel content of most of these springs is much smaller than that of acid vitriol springs represented in the previous papers.

Table 2.

Type of mineral spring	Number of samples	Nickel content (γ/l.) Maximum	Minimum	Median
Acid hydrogen sulphide spring	3	<2	<2	<2
Acid vitriol spring	17	9.38×10^3	4.1_5	133
Carbonate spring	2	1.78	0.78	1.28
Simple cold spring	1	—	—	6.7_5
Ikaho (Iron carbonate spring+Bitter spring)	1	—	—	3.7

(5) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23**(1937), 78.

On the other hand, it seems that there is a relation between the atomic ratio of nickel to iron and the type of mineral spring. The atomic ratio of nickel to iron of each type is summarized in Table 3, together with that of the acid vitriol springs.

Table 3.

Type of mineral spring	pH	Ni/Fe -atomic ratio		
		Maximum	Minimum	Median
Acid hydrogen sulphide spring	1.5	$<1.32\times10^{-4}$	$<0.32\times10^{-4}$	$<0.51\times10^{-4}$
Acid vitriol spring	2.4*	16.21×10^{-4}	0.67×10^{-4}	1.35×10^{-4}
Carbonate spring	6.4	—	—	0.57×10^{-2}
Simple cold spring	6.7	—	—	2.6×10^{-2}
Ikaho (Iron carbonate spring +Bitter spring)	—	—	—	7.8×10^{-4}

* Median.

The data of nickel content of mineral springs other than acid vitriol springs are too deficient to discuss the relation of the atomic ratio of nickel to iron and the type of mineral spring. The difference between each type, however, is so marked that we can find a relation thereof. The atomic ratio of acid vitriol springs shows to be smaller than that of mineral springs of other types, and than either that of the abundance ratio in the earth crust or that of the igneous rocks. On the contrary, the atomic ratio of nickel to iron of the carbonate spring nearly corresponds to that of the igneous rocks. Even it, however, is remarkably small in comparison with the atomic ratio of nickel to iron in the sea water (about 1/20) obtained by V. M. Goldschmidt[6]. The simple cold spring, Mamegara-hudō-yu, shows the remarkably great atomic ratio of nickel to iron, but

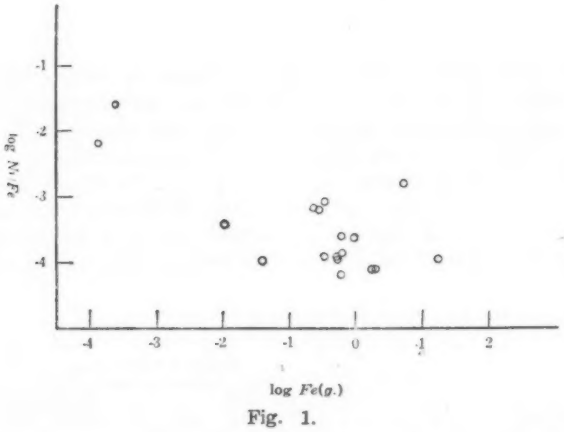

Fig. 1.

(6) V. M. Goldschmidt, *Fortschr. Mineral. Krist. Petrog.*, **17** (1933), 112.

it is considered to be exceptional, because it contains a larger quantity of nickel than others of the same type. The idea would be verified by the fact that nickel is detected spectroscopically in this spring contrary to most of the simple cold springs in which no nickel is detected by the same method. Since the spring, on the other hand, contains iron in the ordinary quantity to most of the simple cold springs, the atomic ratio of nickel to iron of the former shows greater than that of the latter. Consequently, most of the simple cold springs seem to be of smaller atomic ratio of nickel to iron than the spring, Mamegara-hudō-yu.

Service water of Tokyo, gives the intermediate value of the igneous rocks and the sea water.

In Fig. 1, the relation between the iron content and the atomic ratio of nickel to iron is shown. The smaller the iron content, the greater is the atomic ratio of nickel to iron.

Fig. 2 shows the relation between the pH value and the atomic ratio of nickel to iron. In general, the greater the pH value, the greater is the atomic ratio of nickel to iron.

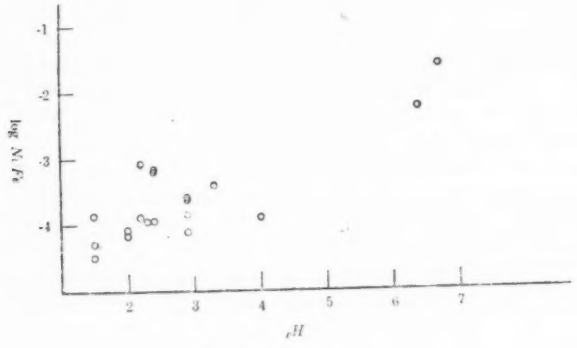

Fig. 2.

The fact that the sea water shows the greatest atomic ratio of nickel to iron is explained by the investigation on the distribution of nickel between the solution and the deposit. It has been confirmed in the experiment on the mineral springs, Kinkei and Tentoku, that the ferric oxide produced from the mineral waters by being kept on standing is generally accompanied by little nickel. In the present study the same fact is found in the mineral waters of Ikaho. The atomic ratio of nickel to iron, both of the filtrate and precipitate, is summarized as shown in Table 4.

Table 4.

	Ni/Fe -atomic ratio	
	Filtrate	Precipitate
Kinkei	7.7×10^{-4}	0.082×10^{-4}
Tentoku	17.9×10^{-4}	1.7×10^{-4}
Ikaho	3.4×10^{-2}	3.9×10^{-4}

Moreover, the fact that the ocherous deposit of Ikaho contains a very minute quantity of nickel, and that its atomic ratio of nickel to iron is extremely smaller than the atomic ratio of the waters, shows the same phenomenon occurs in nature as in the laboratory.

In the weathering zone, iron of the hydrosphere deposits accompanied by little nickel, and therefore, it produces ocherous deposits poor in nickel, while nickel is transported with the surface waters, increasing the atomic ratio of nickel to iron with the deposition of ferric hydroxide. It finally enters into the sea, where since most of the rest of iron deposits, the atomic ratio of nickel to iron becomes the greatest.

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